Eco-friendly Synthesis of $PbMnO_3$: Its photocatalytic Activity for Removal of Orange G Dye

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ABSTRACT

Herein we report the simple one-step eco-friendly synthesis of $PbMnO_3$ by using mechanochemical method. The synthesized catalyst was characterized by various investigative techniques like UV-DRS, FTIR, XRD, SEM, EDAX, TEM, and BET .The product corresponds to average particle size of nm 187 nm by TEM images. Photocatalytic activity of $PbMnO_3$ was studied by photodegradation of Orange G dye under UV-Visible light irradiation. The results indicate that the UV-Visible light stimulates a photochemical reaction and successfully complete mineralization of Orange G dye.

KEYWORDS: Green chemistry, Photocatalyst, Photodegradation, Orange G dye

INTRODUCTION

From last few years, the use of perovskite type compound as catalyst has been deeply investigated. Perovskite oxide nanocrystals have important properties in ferroelectricity, piezoelectricity, dielectricity, ferromagnetism, and multiferroics. Most of the properties of pervoskite oxides are related to the network of BO_6 octahydra [1] and the state of B-site cations [2, 3], whereas brownmillerite ($A_2B_2O_5$), where A is large s, d or f block cation and B is transition metal cation, is a kind of oxygen deficient pervoskite like three dimensional framework of corner shearing BO_6 octahydra which are formed by the deficiency of oxygen during the formation of the structure [4, 5]. Both pervoskite and brownmillerite have been studied widely [6, 7]. Perovskite type oxides have many practical applications owing to its excellent physical and chemical properties and have been shown to have high catalytic activity for the oxidation of carbon monoxide, methane, propane, hexane and Toluene. Thus, it can be used as a catalyst for combustion, automobile exhaust, and waste gaspurification. Apart from this, it can be used as an electrode material for solid-electrode fuel cells and gas sensors [3].

Synthetic dyes are toxic chemicals, which can generate intensive colour and are harmful to the environment. Aquatic life is largly affected due to presence of these dyes in aqueous medium. Because of their incomplete use and washing operations considerable amount of dyes have been noticed in textile wastewater [8]. The dyes were detected in dissolved or in suspension state in the wastewater [9]. The distict colour of water has adverse effect on aquatic system due to presence of dyes and pigments. Mineralization of organic water pollutants using interaction between ultraviolet radiation and semi-conductor catalysts has a strong potential as it has been widely demonstrated in the recent years [10]. Visible light-induced photocatalysts have received considerable attention because visible light occupies

the main part of solar light. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. The past two decades have witnessed intensive studies within light-induced mineralization of hazardous organic pollutants with use of TiO_2 photocatalyst [11–15]. Alton and Ferry [16] used SiW_2O_4 as photocatalyst for the photocatalytic degradation of acid orange dye.

In the present study we have used mechanochemical method for the synthesis of $PbMnO_3$ photocatalyst. Present method is superior than methods available in literature. The significance of this method is that, it is eco-friendly, requires less time and easy to workup. The Product obtained was characterized by various analytical technique and is further checked for its photocatalytic activity for degradation of Orange G dye.

EXPERIMENTAL

Material and Method

In this method, equimolar mixture of analytical grade PbO and MnO_2 was grinded with mortar and pestle to acquire fine powder for 20 min and calcinated at 500 ^{0}C for 3 h. Again the obtained powder was further calcinated at 800 ^{0}C following milling after each interval of three-hour time. The rise in temperature of muffle furnace was programmed at the rate 10 ^{0}C/min from one temperature to the subsequent temperature for 12 h. After heating at 500 ^{0}C the material was cooled and grounded with gap of 1 h using mortar and pestle. Later on, the ground material was further heated at 800 ^{0}C for another 12 h. Finally, polycrystalline powder of $PbMnO_3$ obtained was used for further characterization and for degradation of the dyes.

Characterization of PbMnO3 photocatalyst

The vibrational frequency of the synthesized catalyst was studied by FTIR-8400S (Shimadzu) in the range of 400–4000 cm-1. The structural properties of the material were studied using X-ray diffractometer-DMAX-2500 (Rigaku) with Cu-Ka radiation, having $\lambda = 1.5406$ A. The optical property of the synthesized product was studied by using UV-visible Spectrophotometer- λ -950 (PerkinElmer). $PbMnO_3$ photocatalyst was scanned over wavelength range of 200–800 nm. The surface morphology and chemical compositions of synthesized catalyst was analyzed using a Scanning Electron Microscope-JSM-6300 (JEOL) coupled with an energy dispersive spectrometer ED-2300LA (JEOL). TEM images was recorded on CM-200 (Philips). The surface area of the material was measured by Brunauer–Emmett–Teller Surface Area (BET) analysis, by N_2 adsorption-desorption isotherm, was carried out on Quantachrome Autosorb Automated Gas Sorption System Autosorb-1, NOVA-1200 and Mercury Porosimeter Autosorb-1c.

Photocatalytic activity

Photocatalytic performance of synthesized $PbMnO_3$ was evaluated by studying degradation of Orange-G dye. For detail study we have performed three experiments. In one set 50 mL 20 ppm solution of a dye was irradiated using 0.8 g of photocatalyst, $PbMnO_3$, in UV-Visible light. The decrease in absorbance due to mineralization was recorded on double beam UV–visible spectrophotometer (Systronics) after every 10 min.By optimizing the condition for degradation of Orange G dye. 0.8 g of the

photocatalyst was utilized in 50 mL 20 ppm of the dye solution under same environment.The change in colour of dye solution with time is measured in terms of absorbance using spectrophotometer.

RESULTS AND DISCUSSION

Characterization of $PbMnO_3$

The FT-IR spectrum of the synthesized $PbMnO_3$ catalyst is depicted in Fig. 1. The synthesized $PbMnO_3$ photocatalyst was confirned by vibrational frequency band at 432 and 569 cm^{-1} due to the presence of Pb–O and frequency around 393 and 600 cm^{-1} due to the presence of Mn–O.

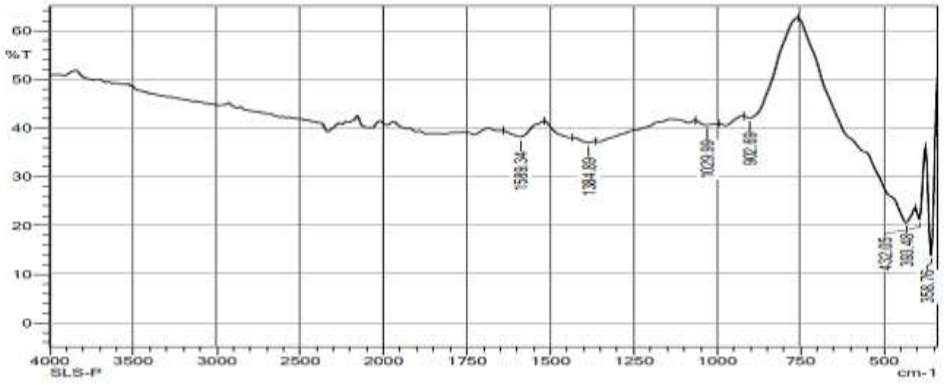

Fig. 1: FT- IR spectrum of $PbMnO_3$

Figure 2 shows XRD pattern of $PbMnO_3$ powder formed after heating. The crystal structure of $PbMnO_3$ is cubic in nature-and all the d-line patterns well match with JCPDS data.

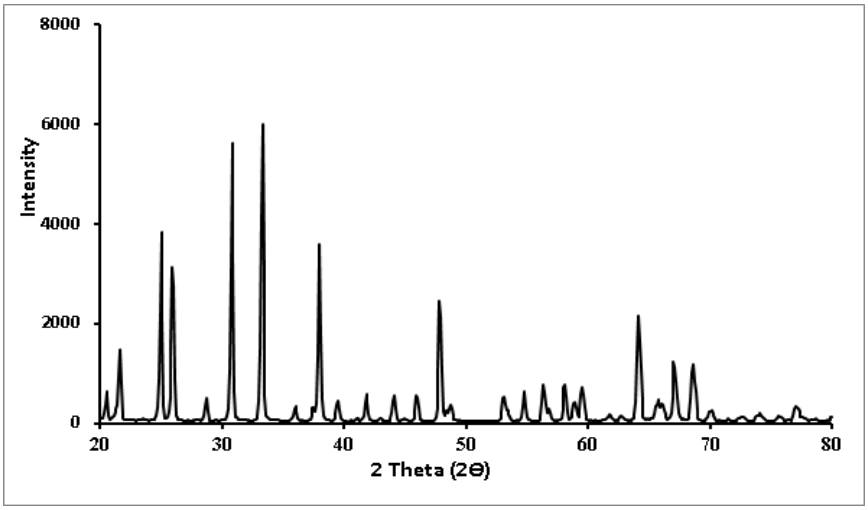

Fig. 2: XRD pattern of $PbMnO_3$ photocatalyst

Figure 3 represents the UV–visible diffused reflectance spectrum of the synthesized $PbMnO_3$ photocatalyst. The UV-DRS of the $PbMnO_3$ has absorption edge cut-off at 345 nm with corresponding band in the visible region. The band gap energy ($Eg = hc/\lambda$) for the compound was found to be 3.739 eV. The broad absorption edge shoulder in the curve confirms the formation of $PbMnO_3$.

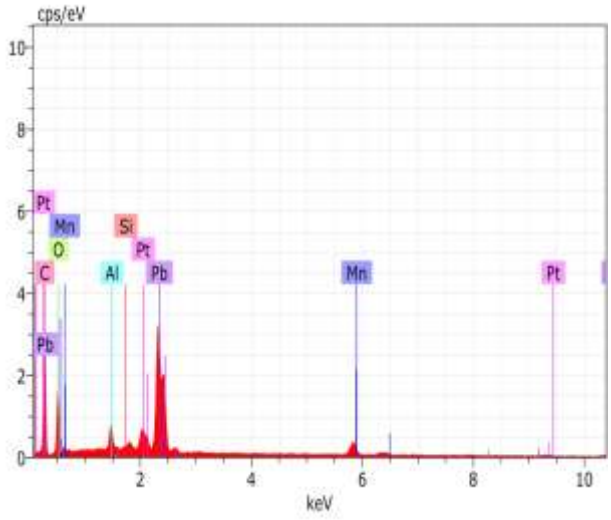

Fig. 3: UV–visible DRS of $PbMnO_3$

Scanning Electron Microscopy was used to see the surface morphology of synthesized $PbMnO_3$ (Fig. 4). The SEM image shows that the particles are agglomerating with each other. The EDAX data furnishes elemental composition in conformity with the respective molar proportions taken.

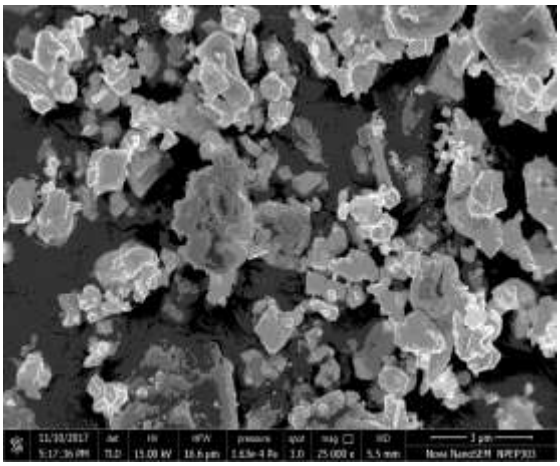

Fig. 4 SEM and EDAX analysis of $PbMnO_3$ photocatalyst.

The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponding to $PbMnO_3$ is shown in Fig. 5. The TEM reveals that, the particles are cubic. The dark spot in the TEM micrograph of PbMnO3 as SAED pattern associated with such spots confirms cubic structure of $PbMnO_3$ and is in total agreement with the XRD data. The average size of the $PbMnO_3$ was found to be 187 nm.

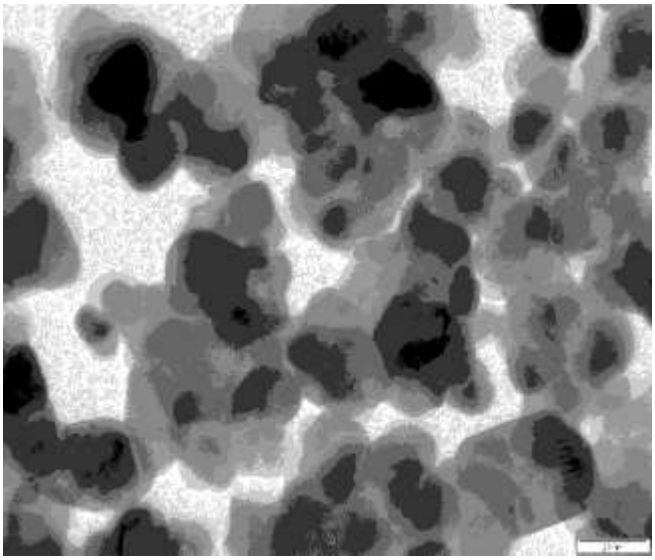

Fig. 5: TEM and SEAD image of $PbMnO_3$ photocatalyst

Figure 6 depicts N_2 adsorption -desorption isotherm for synthesized $PbMnO_3$ photocatalyst. It shows the typical IV N_2 adsorption- desorption isotherm with H1 hysterisis which indicate that sample preserve cylindrical mesopores nature of $PbMnO_3$ photocatalyst. The BJH pore size distribution demonstrates that a narrow pore diameter range. Based on the N_2 adsorption-desorption isotherms, surface area (S_{BET}) is 187.9 m^2/g, the average pore volume (Vp) and pore diameter (dp) were 0.0106 cc/g and 18.88 A^0 respectively.

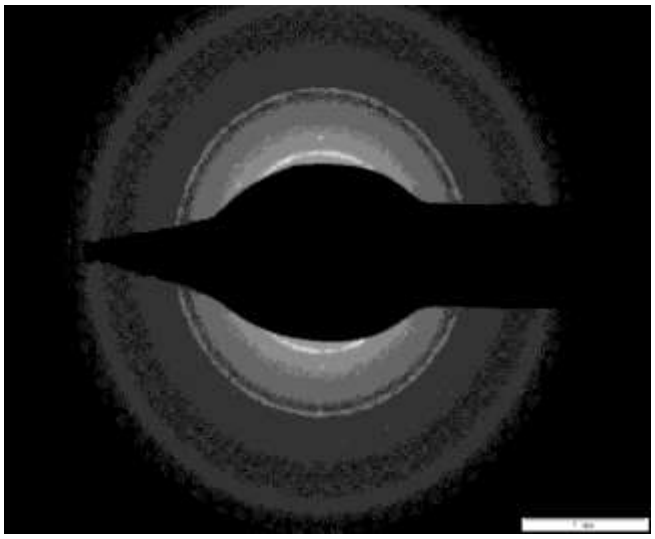

Fig. 6: BET surface area of $PbMnO_3$ photocatalyst*

Photocatalytic property of $PbMnO_3$

Photocatalytic property was evaluated by photodegradation of Orange G dye. The photodegradation of the dye was studied by measuring the absorbance after every 30 min on double beam spectrophotometer (Systronics).

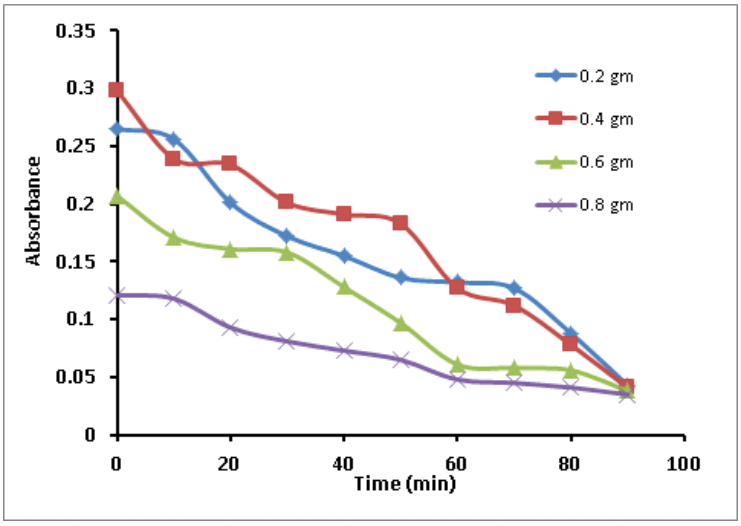

Fig. 7: Effect of amount of catalyst on degradation of dye

Figure 7 shows with increased amount of photocatalyst enhance the degradation of Orange G dye. In the Fig. 6, 0.6 gm of catalyst indicates the rapid degradation of dye. This may be due to increase in amount of the photocatalyst, which increases ejection of number of photons and electrons in the conduction band and in the valence band, respectively. Effect of change of concentration of dye was shown in fig. 8.

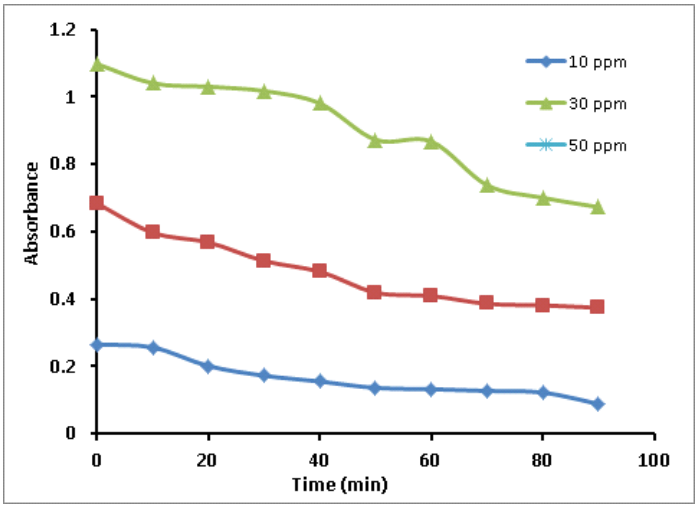

Fig. 8: Effect of concentration of dye solution on degradation using $PbMnO_3$ photocatalyst

The variation of degradation efficiency could be understood by the following mechanism (fig.9). Under the irradiation of $PbMnO_3$ particles, PbMnO3 works as electron scavenger, which may react with the superoxide species and prevent the holes / electrons (h^+/e^-) recombination and thus increases photo-oxidation efficiency. The degradation efficiency increases upto 86.56 % is obtained. The possible reaction is represented below:

$$PbMnO_3 + O^{2-}(ads) \rightarrow Cu^{+} + O_2(ads)$$

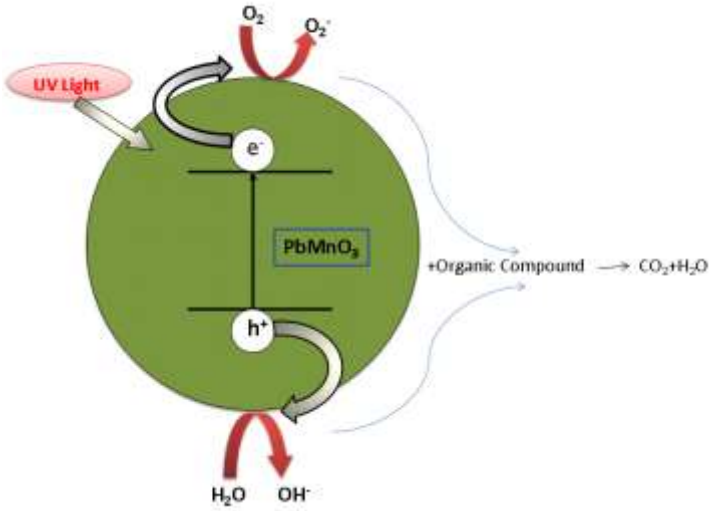

Fig. 9: Mechanism of dye degradation

CONCLUSIONS

The photocatalyst $PbMnO_3$ was synthesized by green chemistry approach using mechanochemical method. Synthesis of $PbMnO_3$ and degradation of Orange G dye were carried out without affecting aquatic life. The band gap energy of the photocatalyst was 3.739 eV with average particle size 187 nm. The TEM micrograph and SAED pattern associated with spots reveals occurrence of cubic $PbMnO_3$ and is in total agreement with the XRD data. $PbMnO_3$ photocatalyst was effectively used for degradation of Orange G dye.

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